Introduction

Today, continuous hot-dip galvanized sheet product is manufactured almost exclusively with a coating that contains a small amount of aluminum. This practice has been in place for many years, and in fact, the technology associated with the use this small amount of aluminum is what promoted the popularity of galvanized sheet. The addition of aluminum is not made to enhance the corrosion performance. Its use is strictly to improve the user’s ability to form the product and maintain good adhesion of the coating during the forming operations. This GalvInfoNote explains the influence of aluminum and why its use is so important to the successful use of continuous galvanized sheet.

Metallurgy of the Coating

Continuous galvanized sheet is made by immersing steel sheet, as a continuous ribbon, into a molten bath of zinc. The process is explained in detail in GalvInfoNote #2. Both sides of the steel sheet are very clean and free of surface oxides when it is introduced into the coating bath. The cold rolled steel is usually annealed at high temperatures (in excess of 1200°F or 650°C) ahead of the coating bath and then cooled to approximately 875 - 925°F (470-490°C) at the point where it enters the coating bath. The zinc, which melts at 787°F (419°C), is typically heated to about 870°F (465°C). Fortunately, the steel sheet has sufficient high-temperature strength so that it can be pulled through both the annealing furnace and the molten zinc bath without tearing or deforming.

During the time that the sheet is immersed in the bath (on some coating lines, as brief as 1 second), the steel and molten zinc react metallurgically. What happens? The surface atoms on the steel sheet, which are still in the solid state, and the atoms of zinc, in the molten state, become mixed. The process whereby this occurs is called diffusion. In fact, atoms of zinc move in the direction of the steel and the atoms of iron in the steel migrate towards the molten zinc. The result is the formation of a solid “mixed” layer between the steel and the molten zinc. This layer contains zinc and iron atoms in specific proportions forming a specific intermetallic compound. As is well known, the mixing of atoms of different metals is called alloying. Thus, the diffusion zone is called an intermetallic alloy. It is this zone that provides the intimate bond between the steel and the zinc coating.

As the steel is pulled from the bath of molten zinc, the strip is allowed to cool. The molten zinc outer layer, which is adhering to the steel as it is pulled at high speeds from the molten bath, solidifies as the strip is cooled below the melting point of the zinc (787°F or 420°C). Thus, the final product (“galvanized sheet”) consists of: the steel core, the zinc outer layer, and the intermetallic alloy layer which is present between the steel and the zinc coating. At high magnification, the coating would look similar to that in the following photomicrograph, if the zinc bath was aluminum free.
The above intermetallic alloy layers, as stated previously, are a mixture of zinc and iron atoms. They provide a high degree of bonding between the steel and the zinc outer coating. Unfortunately, these alloys exhibit very poor ductility, i.e., they are very hard and brittle. When the user/customer wants to form the sheet into a shape of some sort, there is a high tendency for shear cracks to develop in the alloy, and the zinc coating flakes off. This behaviour seriously limits the ability to form the sheet into any shape that requires a high degree of forming such as a drawn cup, a small-radius roofing panel, a tight lockseam, or a highly stretched automotive fender.

Overcoming the Brittle Alloy Layer

An alloy layer is vital to get good bonding between the steel and the molten zinc. Also, the alloy layer has to be continuous (on the entire surface area of the sheet surface) in order to have a coating that is free from pores. Without interfering with the formation of the alloy bond zone, how can the performance be improved so that forming into intricate shapes is feasible?

Over 50 years ago, it was discovered that the addition of a small amount of aluminum to the coating bath is a perfect answer to this problem. Initially, many issues related to the science of why aluminum worked so effectively were not understood, but it was observed that the addition of aluminum to the zinc coating bath made the alloy layer very thin compared that from an aluminum free bath. In fact, the aluminum acts as an inhibitor that greatly slows down the zinc-iron reaction rate. This thinner alloy layer allows the users of the product to shape the sheet into many complex shapes without loss of coating adhesion. The thin alloy layer is not prone to the development of large internal shear cracks, and as a result, users are able to form the sheet without any degradation in the adhesion of the coating.

The use of aluminum, at a level of approximately 0.15%, became the standard for the galvanizing baths in commercial use. To this day, an aluminum addition practice is used. There is a much better understanding of the science associated with the use of aluminum, so that today the aluminum concentration is much more closely controlled. Some manufacturers use perhaps as high as 0.20 to 0.25% aluminum, but most commonly, the standard practice involves the use of about 0.15 to 0.19%.
Although the addition of this small amount of aluminum has a pronounced effect on the ability to form galvanized sheet, it does not have much effect on other attributes of the product. For example, the effect on bulk corrosion behaviour is insignificant. The amount of aluminum can affect issues such as spot welding, soldering, white rust occurrence, but in all cases, the effect is minimal. These effects are insignificant in comparison with the beneficial effect that aluminum exerts on the ability to form the sheet and still maintain good adhesion of the coating.

Why Aluminum Changes the Alloy Layer

How can this small amount of aluminum have such a pronounced influence on the alloy layer growth rate? The answer is that, when aluminum at this level is added to the coating bath, the normal zinc-iron alloy compounds, e.g., FeZn$_7$, that are known to grow at a fast rate, are no longer the stable compounds. Aluminum has a greater affinity for iron than zinc, so that instantly upon the steel entering the coating bath, the stable intermetallic compound that forms is not a zinc-iron compound, but an aluminum-iron compound, i.e., Fe$_2$Al$_5$. This alloy layer is extremely thin and retards the zinc-iron reaction. By the time the strip leaves the bath (1-3 seconds) some zinc is taken into this alloy layer, but the nature of the alloy compound is changed tremendously from what occurs in the absence of aluminum. It is a very thin, ternary intermetallic layer composed of approximately 45% Al, 35% Fe and 20-35% Zn (Fe$_2$Al$_{5-x}$Zn$_x$). Instead of the high diffusion rate that occurs when liquid zinc and solid iron begin to form a binary, FeZn$_7$ alloy in aluminum-free baths, the diffusion rate is now dependent on the diffusion characteristics of zinc through the barrier created by the aluminum-iron compound. The reaction rate between zinc and iron is decreased dramatically, and the net result is that the final thickness of the alloy layer is much less that when the thickness is dependent on the diffusion rate across a growing zinc-iron alloy zone.

The nature of the alloy layer, when aluminum is added to the galvanizing bath, is shown in the following figure. The alloy layer is the pencil-thin line seen in this photograph. When the alloy layer is this thin, the net result is that the coated sheet can be bent or shaped into many useful shapes without worrying about loss of coating adhesion.
What a discovery! This development single-handedly allowed the growth of a large industry; the production of hot-dip galvanized sheet in a continuous operation. Today, galvanized sheet is used for many, many applications including those that require the sheet to accommodate very severe forming.

**Aluminum Content in the Coating**

Recall that for the production of galvanize, the coating bath contains 0.15-0.17% aluminum. When the coatings made from such a bath are later analyzed, they are found to have a bulk aluminum content of from 0.25 to 0.40%. How does this happen? The answer lies in the strong affinity aluminum has for iron. The initial alloy that forms is Fe$_2$Al$_5$; by weight over 55% aluminum. The aluminum actually concentrates at the steel zinc interface and is taken out of the bath with the strip. The bulk of the aluminum in the coating is therefore tied up at the interface. The amount of this interface intermetallic alloy is independent of coating weight (mass). This is why a lighter coating weight (mass) contains a higher overall percentage of aluminum. The rate of aluminum addition to the bath must take into account situations that cause the aluminum removal rate to vary, e.g., coating light gauge sheet (high surface area) with a thin zinc coating removes aluminum at a much higher rate than running heavy gauge sheet with a thicker coating. There are other factors that control the amount of aluminum in the coating, such as: immersion time, aluminum addition rate, zinc bath temperature, and steel type. A discussion of these goes beyond the scope of this GalvInfoNote.

**Aluminum in Galvannealed Coatings**

Since the presence of aluminum dramatically restricts the growth of the alloy layer, what is done when attempting to make galvannealed product? Remember, the production of galvanneal involves the growth of the zinc-iron alloy compounds throughout the coating thickness, so that the final product has approximately 9 to 10% average iron content throughout the coating. Refer to GalvInfoNote #5 for a complete description of how galvanneal is made.

The reheating of the strip to necessary to produce galvanneal restarts the zinc-iron diffusion reaction. Within seconds the heat breaks down the aluminum-iron inhibition layer that formed in the zinc bath. For this to happen in the time available is an issue of aluminum control that was unheard of in the early days of continuous galvanizing. Remember, the production of galvanneal requires that the zinc and steel alloy readily; at a rate high enough so that complete diffusion of iron throughout the coating can be accomplished in a reasonable timeframe (allowing production of galvanneal to be done at economical rates). What has been learned is that, if the aluminum concentration in the coating bath is reduced to less than 0.15% (in the range of 0.12 to 0.14%), there is enough zinc in the ternary alloy layer so that, with the heating, complete mixing between the zinc coating and the steel can be accomplished in a matter of seconds.

A manufacturer who makes both galvanize and galvanneal products on the same coating line can use approximately 0.15 to 0.19% aluminum for galvanized production, and then allow the aluminum level to drop to less than 0.15% to make galvanneal. In practice, this is not as easy as it appears, in that the transition needs to be accomplished in a rapid timeframe. For this, precise control is needed, requiring precise measuring capabilities.
Summary

The above description of the influence of aluminum in the galvanizing bath indicates the importance of this discovery. Today, lines throughout the world use aluminum in their galvanizing baths. Through the years, much has been learned about the influence of aluminum, and the science behind its success, which, in turn, has greatly influenced the processing practices in place today. Most assuredly, though, the use of aluminum to reduce the thickness of the alloy layer is the one development that makes continuous galvanizing a reality.